

## PATENT SPECIFICATION

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## (54) IMPROVING THE QUALITY OF OCTENES

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process of converting highly branched octenes into lower branched octenes suitable for further use in chemical reactions.

In particular the invention relates to the treatment of octenes as obtained from the polymerization of lower olefins. Octenes are an important feed for the preparation of chemical intermediates, such as plasticizers made by the esterification of alcohols prepared by the OXO-process. For such end-use products high quality octenes are required, containing at most minor amounts of triple branched isomers. A suitable process to prepare octenes is the polymerization of lower olefins by the so-called UOP process under the action of a phosphoric acid containing catalyst. The UOP is described in "Advances in Catalysis", Vol. 8, 1956, pp 219—238 under the heading "Polymerization of Olefins from Cracked Gases".

The feed may be a mixture of butenes or a mixture of propylene and butenes (in which case octenes form byproducts in the heptane preparation).

The conventional UOP-process as applied to the above mixtures consists of the polymerization step followed by fractional distillations to separate various olefins formed ( $C_4$  to  $C_{12}$ ). The octenes which are present in the mixture of the higher olefins or the octenes recovered from such mixtures contain normally substantial amounts of triple branched isomers, which make them less suitable for the preparation of high-quality end-products, as already mentioned above.

It is the principal object of the present

invention to provide a process whereby octenes containing substantial amounts of triple branched isomers are converted into better quality octenes with only a minor amount of triple branched isomers. It is a further object of the present invention to provide such a process which is applicable to olefin mixtures containing octenes, which are obtained by the UOP polymerization process.

Accordingly the invention provides a method of upgrading the quality, of highly branched octenes containing substantial amounts of triple branched isomers into octenes containing no more than 15% triple branched isomers by contacting the octenes or an olefin mixture containing the octenes with an acidic catalyst at a temperature from 300° to 500°F. and at a pressure of 100 to 1200 psi. The space velocity may vary within wide limits depending on the activity of the catalyst. Although a great variety of acidic catalysts are suitable for use in the practice of the invention a phosphoric acid-containing catalyst, e.g. kieselguhr impregnated with phosphoric acid is generally preferred because this type of catalyst gives particularly good results. Another support material may be selected from other conventional carriers. Under the conditions of temperature and pressure specified above, space velocities of 0.1 to 2.0 US gallons of liquid fed per hour per pound of catalyst (USGH/Lb) are permitted.

In order to maintain the activity of the acidic catalyst comprising phosphoric acid, it is advisable to charge the olefin feed with water vapour before contact with the catalyst, e.g. with 200 to 4000 ppm of water vapour.

Injection of water into the feed or contacting the feed with water at an elevated temperature represent convenient means to produce the desired degree of humidity. At the temperatures used in the process of the invention inactivation of the catalyst due to gradual dehydration of the phosphoric acid contained therein would be caused by a dry

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feed passed over the catalyst for long periods of time.

5 The octene feed may in principle be derived from any source, but in practice the octenes will be recovered from the UOP process either for producing heptene with octene as one of the byproducts or by the polymerization of butenes wherein octenes form the main product. The octenes may be subjected to the process of the invention 10 either as an octenes mixture or as a mixture of the octenes with other olefins (lower as well as higher olefins) such as are obtained in the various fractionation steps of the UOP process.

15 Thus in general any olefin mixture containing triple branched octene isomers can be treated according to the process of the invention.

20 This may be utilized in the UOP process which is similar to the present process with the exception of the feed material by recirculating to the main reactor a portion of an octenes-containing stream obtained by distillation of the polymeric products. Polymerization of the lower olefin (propylene, butenes) as well as the selective removal of  $C_8$  triple isomers will take place simultaneously and a product will be obtained with only a minor amount of triple branched octenes.

25 The recirculation ratio will depend on process conditions and may vary within wide limits. If high quality octenes are desired then the amount of octenes to be recirculated will be chosen as high as possible.

30 This recirculation step is of special importance for the UOP process of preparing octenes from butenes.

35 The process of the invention can be applied to octenes of various compositions containing high or moderate amounts of triple branched isomers. In connection with the type of UOP process adopted the amount of triple branched isomers in the octenes may vary from 10 to 40 50%, and even higher.

45 As octenes blend is acceptable as a raw material for the preparation of high quality intermediates and endproducts if the triple branched isomer content is no more than 15% as produced by the process of this invention. It is preferred that such blends contain no more than 10%, and better less than 5%, of triple branched isomers.

50 For high quality intermediates or endproducts the concentration of the triple branched  $C_8$  isomer should be very low and such low concentration can be reached by adapting the reaction conditions, such as choosing a high temperature, active catalyst and low space velocity.

60 If somewhat higher triple branched isomer concentrations are tolerated like endproducts

or the initial amount of the triple branched isomer in the feed is not very high, the reaction conditions can be less stringent.

65 The present process can also be combined with the UOP process, if desirable, by including the reactor for carrying out the present process in the UOP plant before the last fractionation tower. Thus a mixture rich in octenes is first treated in the presence of the acid catalyst before it is fractionated.

#### EXAMPLE 1

75 The reaction was carried out with a UOP composition using a UOP No. 2 catalyst representing Kieselguhr impregnated with phosphoric acid (55—70 wt % phosphate measured as  $P_2O_5$ , remainder Kieselguhr). A tubular reactor was used of a length of 6 feet and an inner diameter of 3/4 inch filled with the catalyst. To avoid an inactivation of are catalyst the feed was charged with water vapour (about 2,500 ppm) by contact with water at 130°F before being passed through the reactor.

85 The feed used and reaction products obtained were analyzed by gas chromatography. The conditions were as follows:

Reactor inlet temperature °F	380	
outlet temperature °F	425	90
Space velocity USGH/LB	0.45	
Pressure, psi	500	

Composition, wt %	Feed	Product	
$C_8-C_{10}$	15.0	9.5	
$C_8$	23.8	12.8	95
$C_7$	19.6	14.5	
$C_6$	19.8	17.0	
$C_5$	21.8	46.2	

Loss of octenes during reaction: 14%.

Skeletal Composition of Octenes	Before reaction	After reaction	
$C_8$ isomers wt %			100
2—2—4 TMP	0.23	—	
2—2 DMH	4.06	4.30	105
2—5 DMH	9.43	13.24	
2—4 DMH	27.65	33.29	
3—3 DMH	4.27	0.88	
2—3—4 TMP	8.22	3.13	
2—3 DMH	17.18	16.37	110
2 Me $C_7$	5.63	5.34	
4 Me $C_7$ and 3—4 DM $C_8$	12.00	11.72	
n $C_8$	0.46	1.07	
3 Me $C_7$	9.03	10.15	115
non identified Triple branched isomers	1.84	0.51	
	8.45	3.13	

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**EXAMPLE 2**

The process as described in example 1 was repeated with another feed material. The conditions were as follows:

5	Reactor inlet temperature °F	355
	outlet temperature °F	440
	Space velocity USGH/LB	0.45
	Pressure, psi	550
	Water in the feed (ppm) approx.	1800

10	Composition, wt %	Feed	Product
	$C_4-C_8$	1.2	1.3
	$C_5$	0.4	1.3
	$C_6$	3.1	4.3
	$C_7$	75.3	50.0
15	$C_8$	4.7	8.3
	$C_{11}$	2.1	4.1
	$C_{12}$	2.6	5.3
	$C_{13}$	8.4	21.4
20	$C_{14}^+$	1.5	3.0
		0.7	1.0

Loss of octenes during reaction: 33.6%.

	Skeletal Composition of Octenes	Before reaction	After reaction
25	2-2-4 TMP		
	wt %	1.81	1.63
	2-2 DMH	3.65	3.52
	2-5 DMH	3.97	9.90
30	2-4 DMH	14.89	26.00
	2-2-3 TMP	9.46	1.28
	3-3 DME	1.51	1.56
	2-3-4 TMP	22.49	7.66
	2-3-3 TMP	2.93	1.14
	2-3 DMH	16.26	17.53
35	2 Me $C_7$	1.56	3.70
	4 Me $C_7$	1.00	3.00
	3-4 DMH	12.51	10.07
	3 Me $C_7$	6.68	8.78
	n $C_8$	1.28	4.13
40	Summary:		
	Unbranched wt %	1.28	4.13
	Single branch	9.24	15.48
	Two branches	52.79	68.68
	Three branches	36.69	11.71

45 This example shows that about 79% of the triple branched isomer of octene has been converted into olefins of a substantially different carbon number distribution.

50 This 79% represents theoretically a loss of 28.8% on the total octenes. Since the total loss of octenes during the reaction is 33.6%

only, then the loss of the other octene isomers is 4.8% illustrating that the conversion of the triple branched isomer is about 6 times higher than of the other octenes.

**WHAT WE CLAIM IS:—**

1. A process for upgrading the quality of highly branched octenes containing substantial quantities of triple branched isomers into octenes containing no more than 15% triple branched isomers, wherein the octenes are contacted with an acidic catalyst at a temperature of 300 to 500°F. and a pressure of 1000 to 1200 psi.

2. A process according to claim 1, wherein the space velocity is from 0.1 to 2.0 USGH/Lb.

3. A process according to claim 1 or 2, wherein the acidic catalyst is phosphoric acid impregnated on a carrier.

4. A process according to claim 3, wherein the carrier is kieselguhr.

5. A process according to any one of the preceding claims, wherein the octene feed is charged with water vapour in an amount from 200 to 4000 ppm.

6. A process according to any one of the preceding claims, wherein the product octenes stream contains more than 10% triple branched isomers.

7. A process according to claim 6, wherein the product octenes stream contains more than 5% triple branched isomers.

8. A process according to any one of the preceding claims, wherein a mixture of octenes with lower as well as higher olefins is treated.

9. A process according to claim 8, wherein the mixture is treated is derived from the fractional distillation of olefins obtained by polymerizing butenes or butenes and propylene using the UOP process.

10. A process according to claim 8, wherein a mixture derived from the fractional distillation of olefins obtained by polymerizing butenes or butenes and propylene using the UOP process is recirculated partly to the polymerization reactor, wherein simultaneously a selective removal of triple branched octene isomers takes place.

11. A process according to claim 1 substantially as described in the Examples.

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